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Myths and Facts About Dense Phase Non-Aqueous Liquid Migration in the Subsurface

In the environmental field, there are four primary groups of compounds of interest which are considered Dense Phase Non-Aqueous Phase Liquids (DNAPLs). These four groups consist of: 1) chlorinated solvents; 2) creosote, coal tar, and other wood preservatives; 3) polychlorinated biphenyls (PCBs); and, 4) chlorinated pesticides. The fate and transport of groups 2-4 differs significantly from the fate and transport of chlorinated solvents in the subsurface. While many of the same principals outlined in this paper apply to groups 2-4, this paper focuses primarily on migration of chlorinated solvents in the subsurface. Unless otherwise noted, references to DNAPL refer to neat chlorinated solvents.

Part of my career was spent consulting on numerous superfund sites in Silicon Valley. Most of this area is swimming in TCE and no one has been successful to date in actually remediating any of these sites. The information presented herein is largely based on my many failures and the lessons learned at these sites. Those of you with a number of years experience will probably remember making the same mistakes. Those of you who came into consulting at a later date will probably think, "what a doofus".

Site Classification

Waste sites at which chlorinated solvents and other contaminants having a specific gravity of greater than 1 (denser than water) are present can generally be divided into three categories:

- **Category 1** – includes facilities where no residual or pooled DNAPL is present. Contaminants were either released as a dilute solute or were released sufficiently long ago that all of the residual DNAPL has dissolved.
- **Category 2** – includes facilities where DNAPL is present and the DNAPL plume is stable (i.e., no longer migrating). The DNAPL plume is either pooled in structural traps or present at residual saturation.
- **Category 3** – includes facilities where DNAPL is present and still migrating.

These definitions aren't widely used in literature, but are used throughout this paper. As you will see, making a determination of the Site Category is important both in determining how we go about characterizing the site and in determining remedial strategies to clean up the site.

My Life History as It Relates to DNAPLs

- 1940 First mass production and use of chlorinated solvents in the U.S.
- 1975 Elvis dies.
- 1988 Chlorinated solvents begin to become a major issue due to several highly publicized groundwater contamination cases. I show up at my client's office in my new Dodge K car with the Miami Vice theme blaring on the radio to discuss the new "state of the art" pump & treat (P&T) system we have installed to remediate the TCE plume at his site. Based on current thinking, I estimate that the remediation will take 5 years to complete. This estimate is based on removing 20 pore volumes of water to effectively dissolve and remove the estimated sorbed mass and dissolved mass of the contaminant. I fail to account for the unknown presence of residual DNAPL in the subsurface.
- 1992 I return to my client's office in my new mini-van, Vanilla Ice blaring on the radio, to discuss why my P&T system is producing excellent mass removal rates but is not cleaning up the plume. I am now painfully aware of the presence of residual DNAPL on the site, which I wrongfully believe is confined to the source area. The contamination appears to be a small source area with a large aqueous phase liquid (APL) plume migrating downgradient. I'm still scratching my head trying to determine why the recovery well network hasn't been entirely successful in preventing the migration of the APL plume, even though my groundwater elevation maps show great capture. I sell the client on a new "state of the art" technology called air sparging/soil vapor extraction (AS/SVE) to remediate the source area.
- 1996 I return again to my client's office in my new SUV with my tail between my legs and Hootie blaring on the radio. I explain that the AS/SVE system is doing a great job in remediating the source area, mass removal rates are 10 times higher than predicted. However, the dissolved contaminant concentrations aren't really dropping in the downgradient APL plume. Why?
- 1998 The client goes bankrupt and they convert his site to a Starbuck's and a new Gap store.
- 1999 I finally figure out what I did wrong. The results of which are presented in the rest of this paper.

What Caused My Continuing Failure?

The primary reason for my continuing failure was a lack of understanding of how DNAPLs migrate in the subsurface. If you read any current textbook, there is generally a diagram showing the DNAPL migrating vertically through the subsurface until it encounters a low permeability layer. It then pools in a depression or structural trap or slowly migrates laterally for a short distance until the DNAPL mass is exhausted and migration stops, leaving behind a tail of DNAPL at residual saturation. The aqueous phase liquid (APL) plume dissolves from the residual DNAPL plume and travels great distances from the site.

I now believe that the text books are wrong (or at least they only tell part of the truth). Before you dismiss me as a heretic, remember that Columbus' third grade text book said, "the world – she's a flat". The current conceptual model for DNAPL migration is not correct and leads to many errors in assessing and remediating DNAPL sites. The following misconceptions about DNAPL migration still widely exist:

- There is a misconception that DNAPL plumes are generally only found in close proximity to the source area and generally travel slowly. DNAPL plumes are capable of migrating at extremely high velocities; often 5 to 100 times faster than the dissolved plume. The DNAPL plume can also travel significantly faster than even the groundwater flow. Therefore, until the DNAPL plume migration ceases, the leading edge of the DNAPL plume will actually be significantly further from the source than the APL plume.
- There is a misconception that DNAPL plumes tend to cease migration shortly after the release is stopped. In reality, the DNAPL plume may migrate for many years following a release. The length of time that a DNAPL plume will migrate is not only a function of the volume released, but is also dependent upon the length of release time and the initial and residual DNAPL saturation. Don't assume that your site is not a Category 3 site just because the waste disposal ceased many years ago.

The Race is On: DNAPL vs. APL

It has been widely demonstrated that hydrophobic contaminants travel at a retarded velocity in the dissolved phase due to sorption to organic materials and other factors. However, the velocity of contaminants migrating in the DNAPL phase is not affected by these phenomena. Rather, the hydraulic gradient is the primary factor in determining the migration velocity of a DNAPL plume. The hydraulic gradient is determined by the slope of the aquitard. The groundwater gradient has only a minimal effect on the DNAPL migration velocity and flow direction. DNAPLs are capable of migrating in the opposite direction of groundwater flow if the aquitard slope is sufficient.

Additionally, the migration rate of many chlorinated solvents is often faster than the groundwater flow rate due to the lower viscosity and higher density of the solvent. Hydraulic conductivity is directly related to fluid density and inversely related to fluid viscosity (Cohen & Mercer, 1993). Take the following example:

Assumptions:

- TCE has been spilled into the subsurface
- The groundwater gradient (i) is 0.05 ft/ft.
- The slope of the aquitard (θ) is the same as the groundwater gradient.
- The hydraulic conductivity (K) is 0.01 cm/sec
- The intrinsic permeability (k) is 0.001 cm^2
- The retardation coefficient for TCE is 5
- The fluid density (ρ) of TCE is 1.464 g/cc.
- The viscosity of TCE (μ) is 0.57 cp
- The formation porosity (η) is 0.3
- The acceleration due to gravity (g) is 9.8 m/sec^2.

To determine the contaminant migration velocity in the dissolved phase:

$$v = \frac{(K^*i/\eta)}{R} = \frac{[(0.01\ \text{cm/sec}\ {}^*0.05)/0.3]}{5} =$$

3.3×10^{-4} cm/sec or 104 meters/year

To determine the DNAPL migration velocity:

$$v = \left\{\frac{(k^*\rho\ {}^*g)}{\mu}\ {}^*\ \theta\right\} / \eta = \left\{\frac{(0.001\ {}^*\ 1.464\ \text{g/cc}\ {}^*9.8\text{m/sec}^2)}{0.57\ \text{cp}}\ {}^*\ 0.05\right\} / 0.3 =$$

4.20×10^{-3} cm/sec or 1,324 meters per year

The transport velocity comparisons were based on advection and retardation only. Longitudinal dispersion effects might cause the migration of the front of the dissolved phase plume to be higher than the mean dissolved plume velocity, but dispersion effects are minimal when compared to the significant difference in the DNAPL plume migration and dissolved plume migration rates.

How to Determine if Your Site is a Category 2 or Category 3 Site

The determination of whether the DNAPL plume is still migrating (Category 3) is extremely important in evaluating strategies for containment and remediation of the site. For example, if the DNAPL plume is still migrating, any effort to contain the dissolved plume through the use of down gradient wells is likely to fail unless this factor is taken into account. As previously discussed, the DNAPL plume doesn't necessarily migrate in the same direction as the groundwater gradient. Even the higher gradients produced by a recovery well network may not be sufficient to prevent a DNAPL plume from migrating.

The overall distance and length of time a DNAPL plume will migrate is related not only to the volume of pure product released, but to the length of time the material was released, the frequency of release, and the initial and residual saturation levels of the DNAPL. For example, all else being equal a NAPL plume resulting from a spill of 10,000 gallons of TCE occurring slowly over a period of 1 year will migrate much further and longer than an instantaneous spill of 10,000 gallons of TCE.

The time required for a DNAPL plume to cease migration may be roughly calculated as follows:

$$T \quad = \quad t * \frac{Sat_{initial}}{Sat_{residual}}$$

Where:

T = Time required for DNAPL plume to cease migration (years)
t = Time over which DNAPL was released (years)
$Sat_{initial}$ = Initial saturation level of DNAPL
$Sat_{residual}$ = Residual saturation level of DNAPL

Admittedly, this calculation is subject to a high degree of uncertainty due, in part, to the uncertainty in estimating the input values. Don't use the calculation with the intent of determining the exact date at which the plume will demobilize. However, if you are working on a site where they ceased discharging in 1988 and the calculation indicates that it will take 90 years for the plume to stabilize, chances are the DNAPL plume is still mobile.

As an example, take the following hypothetical site:

A semiconductor manufacturer dumped waste TCE in a small pond from 1960 to 1975, when the plant ceased operation. The facility generated about 1,000 gallons of TCE per month and the quantity did not vary significantly over the 20 year span. The TCE was dumped more or less on a continuous basis, so the ground beneath the pond stayed pretty saturated with TCE. For this exercise assume a saturation level of 85% while the discharge was occurring. Also assume a residual saturation level of 15% (Schwille, 1988).

T = 15 years * 0.85/0.15 = 84 years
Estimated date = 1960 + 84 years = 2044 a.d.

Since the calculation predicts that natural demobilization will take 84 years (from the inception of discharge), it is highly likely that this DNAPL plume is still mobile.

Field Methods to Assess the Presence of DNAPL

There are many different tests to assess the presence of DNAPL during drilling and sampling. A brief summary of these tests follows. Please call me if you want more specifics/protocols for any of the tests.

- **Visual** – DNAPL globules may be visible upon close examination of the soil core. This method works best for dark-colored DNAPLs such as coal tars and creosote. Chlorinated solvents are difficult to see.
- **UV Fluorescence** - This test involves scanning a soil sample under ultraviolet light. Many DNAPLs and contaminants associated with DNAPLs will fluoresce under UV light.
- **Water Shake Test** – Mix a soil/water slurry in a VOA vial. Shake, Shake, Shake (KC and the Sunshine Band, 1979). Watch for DNAPL at the bottom of the vial after allowing the vial to sit for a while. Better yet, centrifuge the vials.
- **Hydrophobic Dye Test** – Add Sudan IV dye to soil/water slurry in a VOA vial. If DNAPL is present, the dye turns redder than Bill Clinton at a NOW convention. You will get better results if you centrifuge the samples.
- **Flute Liners** - These are very new on the market. They are long socks with absorbent material impregnated with Sudan IV dye on one side and a plastic liner on the other side. You can insert the liner in an open borehole or through a hollow stem or geoprobe casing. The liner is then inverted to expose the absorbent side to the formation. You fill the inside of the sock with water so that hydrostatic pressure presses the sock against the formation. After a few minutes, re-invert the sock while pulling it out of the hole. Cut open the sock at the surface. Anywhere the sock was in contact with DNAPL, the sock turns red (kind of a Shroud of Turin effect). Installing these liners is much easier to do than to describe.
- **OVA/PID** – If you are pegging the OVA or PID, chances are DNAPL is present at that location. Most DNAPLs have a relatively low Henry's Law Constant (i.e., they are only somewhat volatile). Extremely high OVA/PID readings aren't normally registered in the presence of only sorbed contaminants. Also, if you are using a PID remember that the ionization potential of most DNAPLs is higher than gasoline components. Make sure your PID lamp intensity is higher than the ionization potential of the target compound(s). It may be necessary to trade out the 10.2 eV lamp on the PID for a 11.7 eV lamp in order to detect these compounds.

Tests to Determine if a DNAPL is present

1. *Is the distance to the leading edge of the plume consistent with the information known about the release and aquifer characteristics?*

If you know something of the period of discharge for the contaminants and the aquifer characteristics, you should be able to perform a back of the envelope calculation to determine how far you would expect a dissolved phase plume to travel ($x= t*K*i/\eta$). For example, if the leading edge of a TCE plume is 3,000 feet downgradient from the source area and your calculations indicate that it would take 150 years to migrate that far, something is wrong (TCE wasn't in wide spread use until 60 years ago.).

If the plume has traveled much further than predicted, chances are it migrated most, if not all of the distance, as a fast-moving DNAPL plume.

2. *Does the dissolved contaminant plume flow in the same direction as the groundwater?*

As previously discussed, DNAPL plumes travel downslope along the top of the aquitard. This does not always agree with the direction of groundwater flow. It is even possible for the DNAPL plume to migrate directly upgradient from the source area. Many times this discrepancy in flow directions results in what appears to be a kidney shaped dissolved plume or a dissolved plume which appears to bifurcate although there is not explanation when reviewing the groundwater flow patterns.

3. *How were the contaminants released?*

Many times we can determine through our Phase I/Phase II investigations something about how the contaminants were released. In order to accurately detect the presence and predict the migration of a DNAPL plume, it is important to determine not only where the contaminants were released; but, how the contaminants were released (i.e., how long did the discharge period last, what were the typical volumes and patterns for release, in what phase were the contaminants released).

For example, if the contaminants were released as a dilute solute, they will not form a NAPL plume under any circumstances. Take the example that Nick Norocea mentioned, where drip buckets containing water with high PCE concentrations were regularly dumped in the back of a dry cleaner store. This release mechanism will not result in a NAPL plume, no matter how high the dissolved concentrations and no matter how many times they dumped the buckets over the years.

4. *Do the dissolved groundwater concentrations exceed 1 percent of the aqueous solubility for the compound?*

The aqueous solubility of a pure compound in water is determined in the laboratory under controlled conditions. In the laboratory, the compound may exist in only two phases, as a NAPL or dissolved in the water. However, in the field, the compound may exist in a number of phases, including sorbed to the soil or as a soil gas. Particularly, the sorption capacity of the soil significantly affects the effective solubility of the compound in the aquifer. In nature, the dissolved concentrations of a compound rarely approach the solubility limit, even when the water is in intimate contact with a NAPL pool.

In the event that the dissolved concentrations exceed 1 percent of the aqueous solubility of the pure compound, DNAPL is likely present. The equilibrium between sorbed contaminants (in the absence of NAPL) and the dissolved contaminant concentration rarely results in groundwater concentrations exceeding 1 percent of the aqueous solubility. If more than one compound is present, this calculation becomes more complex (the effective solubility of each compound must be accounted for) but is still managable.

5. *Do the vapor phase contaminant concentrations exceed 25% of the saturated vapor concentration?*

Saturated vapor concentrations for chlorinated solvents range from about 0.52 kg/m^3 (TCE) to 2 kg/m^3 (methylene chloride). Saturated vapor concentrations are calculated in the laboratory. The tests are conducted on a 2-phase system (i.e., the test doesn't account for sorption to soil and dissolution of vapors into pore water). Therefore, in the field, actual vapor concentrations observed for vapors in intimate contact with NAPL plumes rarely approach the saturated vapor concentrations. As a rule of thumb, vapor concentrations in excess of 25% of the saturated vapor concentration may be indicative of the presence of NAPL.

6. *Do the contaminant concentrations decrease with distance downgradient from the source?*

Many times un-identified DNAPL plumes will manifest in unexplicable contaminant patterns that don't decrease with distance away from the source. This is because the dissolved phase plume is resulting from the dissolution of contaminants in the NAPL plume. The APL plume will emanate from the NAPL plume as a "cloud" diffusing upward and laterally from the NAPL. Since the APL plume travels at a retarded velocity, the leading edge of the NAPL plume will always preceed the leading edge of the APL plume until months or years after the NAPL plume ceases migration.

7. *Do dissolved contaminant concentrations away from the source area increase with depth?*

Assuming the absence of a vertical gradient, the only vertical component of a migrating APL plume is due to mixing (e.g, diffusion). This generally results in contaminant concentrations that decrease with depth below the water table. For migrating NAPL plumes, the opposite is true. In this case the contaminants are diffusing upward from the NAPL layer and contaminant concentrations generally decrease upward from the confining layer.

Do the contaminant concentrations in the soil exceed the upper threshold concentrations for sorbed contaminants?

The equilibrium relationship between contaminants in the soil, soil gas, and groundwater can be defined using the following equation:

$$Cs = \frac{[K_d * p_b + \eta_w + H * \eta_a]}{p_b} * C_w$$

Where:
K_d = Soil/water distribution coefficient
p_b = Soil bulk density
η_w = Water filled porosity
η_a = Air filled porosity
H = Henry's Law constant
C_w = Contaminant concentration in water
C_s = Contaminant concentration in soil

If the solubility of the pure phase contaminant is inserted in the place of C_w in the above equation, the value of C_s becomes the soil threshold concentration, $C_{s\text{-threshold}}$. Contaminant concentrations above $C_{s\text{-threshold}}$ are likely the result of DNAPL present in the soil sample. This gets more complex if more than one contaminant is present, but it can still be done.

As an example, $C_{s\text{-threshold}}$ for TCE at a typical Florida sandy site might be on the order of 500-750 mg/kg, depending upon the degree of saturation of the sample.

Additional DNAPL Tests for Sites with Active Pump & Treat Systems

8. *Does the contaminant mass removed by P&T or other remedial technologies significantly exceed the initial contaminant mass estimates which were based on dissolved mass plus sorbed mass?*

Many times, we don't know that we have missed a DNAPL plume until after the remedy has been selected and implemented. The mass of contaminants in a DNAPL plume is usually orders of magnitude greater than the sum of the mass of contaminants sorbed to soil, present as soil gas, and dissolved in the groundwater. In the event that the mass removed by a treatment system exceeds the predicted rates by a significant factor, chances are good that a NAPL is present which went undetected during site characterization.

9. *After shutdown of the remediation system do concentrations rapidly rebound?*

Some of the rebound effects after shut down of a remediation system can be explained due to sorbed contaminant mass, but sorption alone cannot explain contaminants rebounding to higher concentrations. After shutdown, contaminants sorbed on the soil/carbon matrix dissolve into the groundwater in order to return the system to equilibrium. In the case of a system that is operated in a pulsed manner, the rebound concentrations should decrease each cycle, unless DNAPL is present.

NNAPLs

In addition to LNAPLs and DNAPLs, it is also possible to encounter mixtures of chlorinated solvents and other pure liquids which are neither lighter than water (LNAPLs) or heavier than water (DNAPLs), but rather are close enough to the specific gravity of water to be neutrally buoyant (NNAPLs). For example, a waste disposal pit might regularly receive both toluene and TCE. Since these compounds are miscible in each other, the resulting mixture will have a specific gravity somewhere between TCE and toluene, depending upon the relative volume of each in the component mixture.

NNAPLs are particularly difficult to characterize because these nearly neutrally boyant compounds may migrate horizontally in the NAPL phase for large distances before sinking to the bottom of the aquifer or exhasting the mass of NAPL as residual saturation. The NAPL plume may remain at mid-depth in the aquifer or may actually rise and fall over the migration distance.

How should you apply this information to PSI's assessments?

1. Always assume that you are drilling in a DNAPL zone unless you know otherwise. Since we have seen that DNAPL plumes can travel great distances, the old "outside-in" approach may not even be effective in avoiding contaminant drag-down or mobilization of contaminants. Take precautions as you would for drilling in DNAPL (e.g., double cased wells). Never drill through a confining layer on the first drilling mobilization. Wait until you get some initial results and can better characterize the site as a Category 1 site.
2. Drilling on a DNAPL site presents many more challenges than the average corner gas station. Don't send the new, snotty-nosed geologist out on these sites. If they accidentally breach a confining layer, you'll wish fondly for the day when you only hit a fiber optic line.
3. In the immortal words of Chevy Chase, "Be the ball Danny" (Caddy Shack, 1984), or in this case "Be the DNAPL". The primary reason that DNAPLs have generally not been detected isn't because we don't have the technology to detect them, its because we have been sampling along pathways that the contaminant would take if it were in the dissolved phase, not along the pathways a pure phase product would move (i.e., we have been using an incorrect conceptual model).
4. In terms of controlling the success of remediating a site, determining the presence or absence of DNAPL is the single most important piece of information you will collect.
5. Don't be too quick to dismiss P&T as a remedial technology. While most consultants continue to slam groundwater P&T as a remedial technology, it is

still a perfectly good technology for remediation of Category 1 sites and plume containment at Category 2 sites. While many of the newer technologies have higher mass removal rates than P&T, they still may not be sufficient to remediate Category 2 sites, and almost certainly will fail to remediate a Category 3 site.

6. Understand that micro heterogeneities in the subsurface often control DNAPL transport. Small changes in permeabilities, root holes or fissures, and structural features can critically affect the flow path of the DNAPL plume. When pricing these jobs, include extra time for drilling and sampling to allow the field geologist to study the lithology in detail.

7. Don't be a doofus! Learn from my mistakes and the countless other consultants who have made the same mistakes. Protect yourself and PSI by thinking about the implications before, during, and after you drill a potential DNAPL site. If you don't have experience on DNAPL sites, contact another STP for assistance or a second opinion.